Set Name side by side	Query	Hit Count	Set Name result set
	DB=USPT; PLUR=YES; OP=ADJ		
L26	l24 and L25	11	L26
L25	accelerator	55842	L25
L24	l22 or L23	16	L24
L23	thiokol lp 31	15	L23
L22	thiokol lp31	2	L22
L21	l14 and L20	4	L21
L20	l15 not L19	4	L20
L19	l14 and L18	3	L19
L18	l15 not L17	3	L18
L17	l15 and L16	4	L17
L16	polybutadiene or butadiene or polyisoprene or isoprene	92317	L16
L15	('4596839'| '3949125'| '3912758'| '5663219'| '3892700'| '3892701'| '4082693')[PN]	7	L15
L14	l12 and L13	17	L14
L13	l1 or polythiol or polysulfide or polysuphide or polythioether	15555	L13
L12	('4596839'| '3949125'| '4144154'| '3912758'| '6518367'| '3892700'| '3892701'| '3931090'| '6344510'| '4082693'| '4433114'| '3864229'| '4454248'| '4100148'| '4094757'| '5663219'| '4020033')[PN]	17	L12
L11	l8 and l10	38	L11
L10	('6518367'| '6344510'| '5157083'| '5663219'| '5852093'| '3892697'| '3892698'| '4596839'| '3951907'| '3949125'| '4144154'| '3844329'| '3912758'| '3862078'| '3719572'| '3754846'| '3892700'| '4942906'| '3892701'| '3931090'| '4176245'| '4082693'| '3894996'| '4433114'| '4200325'| '3879326'| '3879327'| '3864229'| '4454248'| '4100148'| '4094757'| '4020033'| '3644263'| '4303721'| '4182829'| '4512340'| '3622127'| '3968067')[PN]	38	L10
L9	accelerator and L8	50	L9
L8	l1 same L7	122	L8
L7	l2 or l5	155216	L7
L6	l2 same L5	3796	L6
L5	l3 or L4	143099	L5
L4	cross linking or cross linker or cross link or cross linked	83785	L4
L3	crosslinking or crosslinker or crosslink or crosslinked	86629	L3
L2	vulcanization or vulcanizing	18791	L2
L1	thiokol	2971	L1

END OF SEARCH HISTORY

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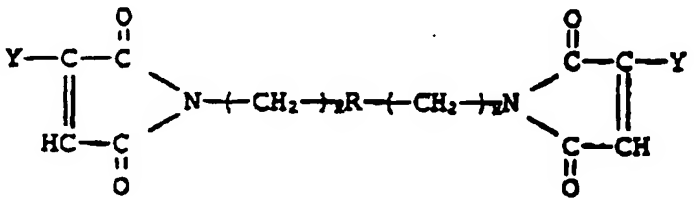
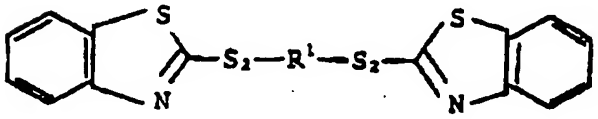
(54) A rubber compound having improved reversion resistance

(57) This invention relates to the discovery that the combination of a bismaleimide compound (I) and a bis benzothiazolyldithio end capped compound (II) provides for excellent vulcanization of rubbers and results in desirable reversion resistant rubbers properties.



(I)



(II)

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Descripti n

Background of the Invention

U.S. Patent 3,979,369 relates to a method for cross-liking rubber with polysulfides. Included in the hundreds of polysulfides listed in this reference are bis benzothiazolyldithio end capped compounds.

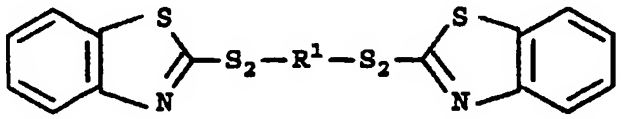
Use of the described bis-benzothiazolyldithio end capped compounds does not yield the desirable anti-reversion properties and reduced heat rise that is sought related to the current invention.

PCT application number PCT/EP94/018 (WO 94/29380 discloses a rubber composition containing citraconimides and itaconimides as anti-reversion coagents.

Summary of the Invention

The present invention relates to a rubber composition containing the combination of:

(a) a bismaleimide and
(b) a bis benzothiazolyldithio compound of the formula:



II

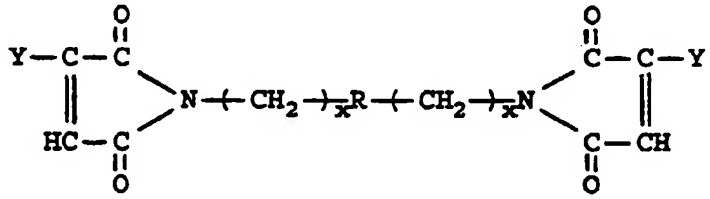
wherein R^1 is selected from the group consisting of alkylene radicals having from 1 to 20 carbon atoms, cycloalkylene radicals having from 6 to 24 carbon atoms and arylene radicals having from 6 to 18 carbon atoms, alkarylene radicals having from 7 to 25 carbon atoms and divalent radicals of the formula:

$$\{R^1\}O\{R^1\}.$$

Detailed Description of the Invention

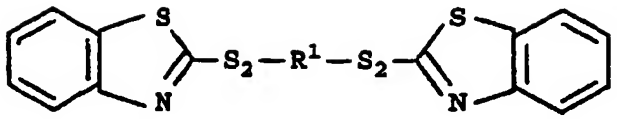
There is disclosed a sulfur vulcanizable rubber composition comprising:

(a) a rubber selected from the group consisting of natural rubber, a rubber derived from a diene monomer and mixture thereof;
(b) from about 0.1 to about 10 phr of a bismaleimide compound of the general formula:



I

wherein R is divalent and is selected from the group consisting of acyclic aliphatic groups having from about 2 to 16 carbon atoms, cyclic aliphatic groups having from about 5 to 20 carbon atoms, aromatic groups having from about 6 to 18 carbon atoms, and alkylaromatic groups having from about 7 to 24 carbon atoms, wherein these divalent groups may contain a hetero atom selected from O, N and S; X is 0 or an integer of from 1 to 3 and Y is hydrogen or $—CH_3$; and
(c) from about 0.1 phr to about 10 phr of a bis benzothiazolyldithio compound of the general formula:



II

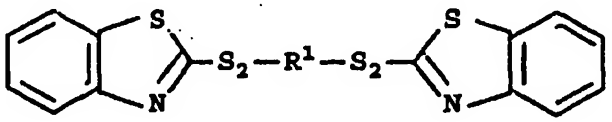
where R^1 is selected from the group consisting of alkylene radicals having from 1 to 20 carbon atoms, cycloalkylene radicals having from 6 to 24 carbon atoms and arylene radicals having from 6 to 18 carbon atoms, alkarylene radicals having from 7 to 25 carbon atoms and divalent radicals of the formula:

$$\{R^1\}O\{R^1\}.$$

The bismaleimide is an essential component in the claimed invention. The bismaleimide is generally present in an amount of from about 0.1 to 10 phr. Preferably, the bismaleimide is present in an amount ranging from about 0.5 to about 5 phr.

Representative of the bismaleimides of formula I and which may be used in the present invention include N,N'-ethylenebismaleimide, N,N'-hexamethylenebismaleimide, N,N'-dodecamethylenebismaleimide, N,N'-(2,2,4-trimethylhexamethylene)bismaleimide, N,N'-(oxydipropylene)bismaleimide, N,N'-(aminodipropylene)bismaleimide, N,N'-(ethylenedioxydipropylene)bismaleimide, N,N'(1,4-cyclohexylene)bismaleimide, N,N'-(1,3-cyclohexylene)bismaleimide, N,N'-(methylene-1,4-dicyclohexylene)bismaleimide, N,N'-(isopropylidene-1,4-dicyclohexylene)bismaleimide, N,N'-(oxy-1,4-dicyclohexylene)bismaleimide, N,N'-(m-phenylene)bismaleimide, N,N'-p-(phenylene)bismaleimide, N,N'-(o-phenylene)bismaleimide, N,N'-(1,3-naphthylene)bismaleimide, N,N'-(1,4-naphthylene)bismaleimide, N,N'-(1,5-naphthylene)bismaleimide, N,N-(3,3'-dimethyl-4,4'-diphenylene)bismaleimide, N,N'-(3,3-dichloro-4,4'-biphenylene)bismaleimide, N,N'-(2,4-pyridyl)bismaleimide, N,N'-(2,6-pyridyl)bismaleimide, N,N'-(m-tolylene)bismaleimide, N,N'-(p-tolylene)bismaleimide, N,N'-(4,6-dimethyl-1,3-phenylene)bismaleimide, N,N'-(2,3-dimethyl-1,4-phenylene)bismaleimide, N,N'-(4,6-dichloro-1,3-phenylene)bismaleimide, N,N'-(5-chloro-1,3-phenylene)bismaleimide, N,N'-(5-hydroxy-1,3-phenylene)bismaleimide, N,N'-(5-methoxy-1,3-phenylene)bismaleimide, N,N'-(m-xylylene)bismaleimide, N,N'-(p-xylylene)bismaleimide, N,N'-(methylenedi-p-phenylene)bismaleimide, N,N'-(isopropylidenedi-p-phenylene)bismaleimide, N,N'-(oxydi-p-phenylene)bismaleimide, N,N'-(thiodi-p-phenylene)bismaleimide, N,N'-(dithiodi-p-phenylene)bismaleimide, N,N'-(sulfodi-p-phenylene)bismaleimide, N,N'-(carbonyldi-p-phenylene)bismaleimide, α,α-bis-(4-maleimidophenyl)-meta-diisopropylbenzene, α,α-bis-(4-p-phenylene) bismaleimide, N,N'-(m-xylylene)bis-citraconimide and α,α-bis-(4-maleimidophenyl)-para-diisopropylbenzene. The preferred bismaleimide is N,N'-(m-xylylene)bis-citraconimide.

The other essential feature of the present invention is the presence of a bis benzothiazolyldithio compound of the formula:



II

wherein R^1 is selected from the group consisting of alkylene radicals having from 1 to 20 carbon atoms, cycloalkylene radicals having from 6 to 24 carbon atoms and arylene radicals having from 6 to 18 carbon atoms, alkarylene radicals having from 7 to 25 carbon atoms and divalent radicals of the formula:

$$\{R^1\}O\{R^1\}.$$

Preferably, R^1 is an alkylene radical having 6 carbon atoms.

The bis benzothiazolyldithio compound is generally present in an amount ranging from about 0.1 to 10 phr. Preferably, such compound is present in an amount ranging from about 0.5 to 5 phr.

Representative compounds of formula II include 1,1-bis(2-benzothiazolyldithio)methane; 1,2-bis(2-benzothiazolyldithio)ethane; 1,3-bis(2-benzothiazolyldithio)propane; 1,4-bis(2-benzothiazolyldithio)butane; 1,6-bis(2-benzothiazolyldithio)hexane; 1,8-bis(2-benzothiazolyldithio)octane; 1,10-bis(2-benzothiazolyldithio)decane; 1,10-bis(2-benzothiazolyldithio)octadecane; 1,18-bis(2-benzothiazolyldithio)octadecane; 2,2'-bis(2-benzothiazolyldithio)oxydiethane; 2,2'-bis(2-benzothiazolyldithio)thiodiethane; 4,4'-bis(2-benzothiazolyldithio)oxydibutane; 1,1-bis(2-benzothiazolyldithio)-1,4-cyclohexanedimethane; 1,4-bis(2-benzothiazolyldithio)b nzene; α,α'-bis(2-benzothiazolyldithio)p-

xylene; 1,2-bis(2-benzothiazolyldithio)cyclohexane; 1,1-bis(2-benzothiazolyldithio)cyclohexane; 1,4-bis(2-benzothiazolyldithio)cyclohexane; 1,4-bis(2-benzothiazolyldithio)naphthalene; 4,4'-bis(2-benzothiazolyldithio)biphenyl; 4,4'-bis(2-benzothiazolyldithio)oxybisbenzene and mixtures thereof.

Examples of rubbers for use in the present invention include substituted and unsubstituted, saturated and unsaturated, natural and synthetic polymers. The natural polymers include natural rubber in its various forms, e.g., pale crepe and smoked sheet, and balata and gutta percha. The synthetic polymers are derived from a diene monomer and include those prepared from a single monomer (homopolymer) or a mixture of two or more copolymerizable monomers (copolymer) when the monomers are combined in the random distribution or block form. The monomers may be substituted or unsubstituted and may possess one or more double bonds, conjugated and nonconjugated dienes and monoolefins, including cyclic and acyclic monoolefins, especially vinyl and vinylidene monomers. Examples of conjugated dienes are 1,3-butadiene, isoprene, chloroprene, 2-ethyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene and piperylene. Examples of nonconjugated dienes are 1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene, dicyclopentadiene, 1,5-cyclooctadiene, and ethyldiene norbornene. Examples of acyclic monoolefins are ethylene, propylene, 1-butene, isobutylene, 1-pentene and 1-hexene. Examples of cyclic monoolefins are cyclopentene, cyclohexene, cycloheptene, cyclooctene and 4-methyl-cyclooctene. Examples of vinyl monomers are styrene, acrylonitrile, acrylic acid, ethylacrylate, vinyl chloride, butylacrylate, methyl vinyl ether, vinyl acetate and vinyl pyridine. Examples of vinylidene monomers are alpha-methylstyrene, methacrylic acid, methyl methacrylate, itaconic acid, ethyl methacrylate, glycidyl methacrylate and vinylidene chloride. Representative examples of the synthetic polymers used in the practice of this invention are polychloroprene homopolymers of a conjugated 1,3-diene such as isoprene and butadiene, and in particular, polyisoprenes and polybutadienes having essentially all of their repeat units combined in a cis-1,4-structure; and copolymers of a conjugated 1,3-diene such as isoprene and butadiene with up to 50 percent by weight of at least one copolymerizable monomer, including ethylenically unsaturated monomers such as styrene or acrylonitrile; and butyl rubber, which is a polymerization product of a major proportion of a monoolefin and a minor proportion of a diolefin such as butadiene or isoprene. The rubber may be emulsion polymerized or solution polymerized.

The preferred rubbers which may be used with the present invention are cis-1,4-polyisoprene (natural or synthetic), polybutadiene, polychloroprene and the copolymers of isoprene and butadiene, copolymers of acrylonitrile and butadiene, copolymers of acrylonitrile and isoprene, copolymers of styrene, butadiene and isoprene, copolymers of styrene and butadiene and blends thereof.

As known to one skilled in the art, in order to cure a rubber stock, one needs to have a sulfur vulcanizing agent. Examples of suitable sulfur vulcanizing agents include elemental sulfur (free sulfur) or a sulfur donating vulcanizing agent, for example, an amine disulfide, polymeric polysulfide or sulfur olefin adducts. Preferably, the sulfur vulcanizing agent is elemental sulfur. The amount of sulfur vulcanizing agent will vary depending on the components of the rubber stock and the particular type of sulfur vulcanizing agent that is used. The sulfur vulcanizing agent is generally present in an amount ranging from about 0.5 to about 6 phr. Preferably, the sulfur vulcanizing agent is present in an amount ranging from about 0.75 phr to about 4.0 phr.

Conventional rubber additives may be incorporated in the rubber stock of the present invention. The additives commonly used in rubber stocks include fillers, plasticizers, waxes, processing oils, retarders, antiozonants, antioxidants and the like. The total amount of filler that may be used may range from about 30 to about 150 phr, with a range of from about 45 to about 100 phr being preferred. Fillers include clays, calcium carbonate, calcium silicate, titanium dioxide and carbon black. Representatives carbon blacks that are commonly used in rubber stocks include N110, N121, N220, N231, N234, N242, N293, N299, N330, N326, N330, N332, N339, N343, N347, N351, N358, N375, N472, N660, N754, N762, N765 and N990. Plasticizers are conventionally used in amounts amounts ranging from about 2 to about 50 phr with a range of about 5 to about 30 phr being preferred. The amount of plasticizer used will depend upon the softening effect desired. Examples of suitable plasticizers include aromatic extract oils, petroleum softeners including asphaltenes, pentachlorophenol, saturated and unsaturated hydrocarbons and nitrogen bases, coal tar products, cumarone-indene resins and esters such as dibutylphthalate and tricresol phosphate. Common waxes which may be used include paraffinic waxes and microcrystalline blends. Such waxes are used in amounts ranging from about 0.5 to 3 phr. Materials used in compounding which function as an accelerator-activator includes metal oxides such as zinc oxide and magnesium oxide which are used in conjunction with acidic materials such as fatty acid, for example, stearic acid, oleic acid, murastic acid, and the like. The amount of the metal oxide may range from about 1 to about 14 phr with a range of from about 2 to about 8 phr being preferred. The amount of fatty acid which may be used may range from about 0 phr to about 5.0 phr with a range of from about 0 phr to about 2 phr being preferred.

Accelerators are used to control the time and/or temperature required for vulcanization and to improve the properties of the vulcanizate. In one embodiment, a single accelerator system may be used; i.e., primary accelerator. The primary accelerator(s) may be used in total amounts ranging from about 0.5 to about 4, preferably about 0.8 to about 2.0, phr. In another embodiment, combinations of a primary and a secondary accelerator might be used with the secondary accelerator being used in a smaller, equal or greater amount to the primary accelerator. Combinations of these accelerators might be expected to produce a synergistic effect on the final properties and are somewhat better than those

produced by use of either accelerator alone. In addition, delayed action accelerators may be used which are not affected by normal processing temperatures but produce a satisfactory cure at ordinary vulcanization temperatures. Vulcanization retarders might also be used. Suitable types of accelerators that may be used in the present invention are amines, disulfides, guanidines, thioureas, thiazoles, thiurams, sulfenamides, dithiocarbamates and xanthates. Preferably, the primary accelerator is a sulfenamide. If a second accelerator is used, the secondary accelerator is preferably a guanidine, dithiocarbamate or thiuram compound.

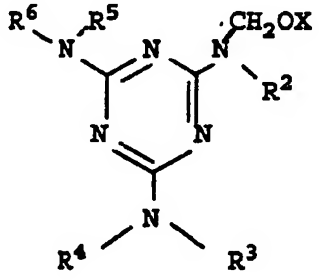
The rubber compounds of the present invention may also contain a cure activator. A representative cure activator is methyl trialkyl (C_8-C_{10}) ammonium chloride commercially available under the trademark Adogen® 464 from Sherex Chemical Company of Dublin, Ohio. The amount of activator may be used in a range of from 0.05 to 5 phr.

The terms "non-productive" and "productive" mix stages are well known to those having skill in the rubber mixing art.

Siliceous pigments may be used in the rubber compound applications of the present invention, including pyrogenic and precipitated siliceous pigments (silica), although precipitate silicas are preferred. The siliceous pigments preferably employed in this invention are precipitated silicas such as, for example, those obtained by the acidification of a soluble silicate, e.g., sodium silicate. Such silicas might be characterized, for example, by having a BET surface area, as measured using nitrogen gas, preferably in the range of about 40 to about 600, and more usually in a range of about 50 to about 300 square meters per gram. The BET method of measuring surface area is described in the Journal of the American Chemical Society, Volume 60, page 304 (1930). The silica may also be typically characterized by having a dibutylphthalate (DBP) absorption value in a range of about 100 to about 400, and more usually about 150 to about 300. The silica might be expected to have an average ultimate particle size, for example, in the range of 0.01 to 0.05 micron as determined by the electron microscope, although the silica particles may be even smaller, or possibly larger, in size. Various commercially available silicas may be considered for use in this invention such as, only for example herein, and without limitation, silicas commercially available from PPG Industries under the Hi-Sil trademark with designations 210, 243, etc; silicas available from Rhone-Poulenc, with, for example, designations of Z1165MP and Z165GR and silicas available from Degussa AG with, for example, designations VN2 and VN3, etc. The PPG Hi-Sil silicas are currently preferred.

A class of compounding materials known as scorch retarders are commonly used. Phthalic anhydride, salicylic acid, sodium acetate and N-cyclohexyl thiophthalimide are known retarders. Retarders are generally used in an amount ranging from about 0.1 to 0.5 phr.

In-situ resins may be formed in the rubber stock and involve the reaction of cashew nut oil modified novolak-type phenolic resin and a methylene donor. The term "methylene donor" is intended to mean a compound capable of reacting with the cashew nut oil modified novolak-type phenolic resin and generate the resin in-situ. Examples of methylene donors which are suitable for use in the present invention include hexamethylenetetramine, hexaethoxymethylmelamine, hexamethoxymethylmelamine, lauryloxymethylpyridinium chloride, ethoxymethylpyridinium chloride, trioxan hexamethoxymethylmelamine, the hydroxy groups of which may be esterified or partly esterified, and polymers of formaldehyde such as paraformaldehyde. In addition, the methylene donors may be N-substituted oxymethylmelamines, of the general formula:



wherein X is an alkyl having from 1 to 8 carbon atoms, R^2 R^3, R^4, R^5 and R^6 are individually selected from the group consisting of hydrogen, an alkyl having from 1 to 8 carbon atoms, the group $-CH_2OX$ or their condensation products. Specific methylene donors include hexakis-(methoxymethyl)melamine, N,N',N"-trimethyl/N,N',N"-trimethylolmelamine, hexamethylolmelamine, N,N',N"-dimethylolmelamine, N-methylolmelamine, N,N'-dimethylolmelamine, N,N',N"-tris(methoxymethyl)melamine and N,N'N"-tributyl-N,N',N"-trimethylol-melamine. The N-methylol derivatives of melamine are prepared by known methods.

The amount of methylene donor that is present in the rubber stock may vary. Typically, th amount of methylene donor that is present will range fr m about 0.1 phr to 10.0 phr. Preferably, the amount of methyl ne donor ranges from

about 2.0 phr to 5.0 phr.

Conventionally, antioxidants and sometim s antioz nants, hereinafter referred to as antidegradants, are added to rubber stocks. Representative antidegradants include monophenols, bisphenols, thiobisphenols, polyphenols, hydroquinone derivatives, phosphites, thioesters, naphthyi amines, diphenyl-p-phenylenediamines, diphenylamines and other diaryl amine derivatives, para-phenylenediamines, quinolines and mixtures thereof. Specific examples of such antidegradants are disclosed in The Vanderbilt Rubber Handbook (1990), pages 282-286. Antidegradants are generally used in amounts from about 0.25 to about 5.0 phr with a range of from about 1.0 to about 3.0 phr being preferred.

The sulfur vulcanizable rubber compound is cured at a temperature ranging from about 125°C to 180°C. Preferably, the temperature ranges from about 135°C to 160°C.

The mixing of the rubber compound can be accomplished by methods known to those having skill in the rubber mixing art. For example, the ingredients are typically mixed in at least two stages, namely at least one non-productive stage followed by a productive mix stage. The final curatives are typically mixed in the final stage which is conventionally called the "productive" mix stage in which the mixing typically occurs at a temperature, or ultimate temperature, lower than the mix temperature(s) than the preceding non-productive mix stage(s). The terms "non-productive" and "productive" mix stages are well known to those having skill in the rubber mixing art.

The rubber composition of this invention can be used for various purposes. For example, the rubber compounds may be in the form of a tire, hose, belt or shoe sole. Preferably, the rubber compound is used for various tire compounds. Such pneumatic tires can be built, shaped, molded and cured by various methods which are known and will be readily apparent to those having skill in such art. Preferably, the rubber composition is used as a wire coat, bead coat, ply coat and tread. As can be appreciated, the tire may be a passenger tire, aircraft tire, truck tire, earthmover, agricultural and the like.

The present invention may be better understood by reference to the following examples in which the parts or percentages are by weight unless otherwise indicated.

Example 1

The rubber stock was prepared in a two-stage non-productive and one-stage productive Banbury mix procedure. All ingredients are listed in Table I. All parts and percentages are by weight unless otherwise noted.

Cure properties were determined using a Monsanto oscillating disc rheometer which was operated at a temperature of 150°C and 100 cycles per minute. A description of oscillating disc rheometers can be found in the Vanderbilt Rubber Handbook edited by Robert O. Ohm (Norwalk, Conn., R. T. Vanderbilt Company, Inc., 1990), pages 554-557. The use of this cure meter and standardized values read from the curve are specified in ASTM D-2084. A typical cure curve obtained on an oscillating disc rheometer is shown on page 555 of the 1990 edition of the Vanderbilt Rubber Handbook.

In such an oscillating disc rheometer, compounded rubber samples are subjected to an oscillating shearing action of constant amplitude. The torque of the oscillating disc embedded in the stock that is being tested that is required to oscillate the rotor at the vulcanization temperature is measured. The values obtained using this cure test are very significant since changes in the rubber or the compounding recipe are very readily detected.

Cure reversion measured using a rheometer can be defined as the incremental time required for a fixed decrease in torque from the maximum value, expressed here for example as M_{HF} -1 Point (time for the torque to decrease 1.0 unit or point below the maximum value M_{HF} Torque). Such cure reversion measurements are defined by G. M. Bristow (NR Technology, 17 (1) 7, 1986).

The following Tables II and III report cure properties that were obtained for the rubber stocks that were prepared. These properties include a minutes to 25 percent of the torque increase (t25), minutes to 90 percent of the torque increase (t90). Table III reports the vulcanizate properties for the rubber stocks cured for 20 minutes at 150°C, 90 minutes at 150°C, 6 minutes at 170°C and 28 minutes at 170°C.

Thus, examination of Table II shows the reversion-resistant behavior at 150°C and 170°C for Perkalink® 900 and BBDTH (Sample 2) used in combination, BBDTH used alone (Control Sample 3) and Perkalink® 900 used alone (Control Samples 4 and 5), versus Control Sample 1 which has no anti-reversion agents added to the compound formulation of Table I. When examining Table II, it is clear that Perkalink® 900 and BBDTH (Sample 2) used in combination provided excellent reversion-resistant behavior when compared to Control Sample 1 which had no anti-reversion agents added to the compound formulation of Table I and was, surprisingly, superior to BBDTH used alone (Control Sample 3) and Perkalink® 900 used alone (Control Samples 4 and 5). Thus, at the 150°C cure temperature, Control Sample 1 had reverted -1 pt in 7 minutes, while Perkalink® 900 and BBDTH (Sample 2) used in combination reverted -1 pt in 97 minutes. BBDTH used alone (Control Sample 3) and Perkalink® 900 used alone (Control Samples 4 and 5) likewise had significantly more reversion versus Sample 2, -1 pt in 30 minutes, -1 pt in 10 minutes and -1 pt in 12.5, respectively, versus -1 pt in 97 minutes for Sample 2 of this invention. A synergistic improvement in reversion resistance is, surprisingly, noted with this combination. At the higher cure temperature of 170°C, Control Sample 1 had reverted -5 pts in 6 min-

utes, while Perkalink® 900 and BBDTH (Sample 2) used in combination had reverted -5 pts in 64 minutes showing a significant improvement in the rate of reversion. BBDTH used alone (Control Sample 3) and Perkalink® 900 used alone (Control Samples 4 and 5) had significantly greater reversion rates versus the Perkalink® 900/BBDTH combination (Sample 2) of this invention, -5 pts in 15 minutes, -5 pts in 8 minutes and -5 pts in 13 minutes, respectively, versus -5 pts in 64 minutes for Sample 2. Again, at the higher cure temperature f 170°C, a synergistic improvement in reversion resistance was surprisingly noted with this combination.

Table I

	Control Sample 1	Sample 2	Control Sample 3	Control Sample 4	Control Sample 5
1st Non-Productive					
Natural Rubber	100	100	100	100	100
Processing Oil	5	5	5	5	5
Carbon Black (N299)	30	30	30	30	30
2nd Non-Productive					
Carbon Black (N299)	10	10	10	10	10
Stearic Acid	2	2	2	2	2
Zinc Oxide	3	3	3	3	3
Productive					
PVI[1]	0.1	0.1	0.1	0.1	0.1
Antioxidant[2]	0.75	0.75	0.75	0.75	0.75
Sulfur	2.25	2.25	2.25	2.25	2.25
CBS[3]	1	1	1	1	1
Perkalink® 900[4]	0	1	0	1	2
BBDTH[5]	0	3.69	3.69	0	0

[1]N-cyclohexylthiophthalimide prevulcanization inhibitor
[2]Mixed aryl-p-phenylenediamines
[3]N-cyclohexyl benzothiazole-2-sulfenamide
[4]N,N'-(m-xylylene)bis-citraconimide
[5]BBDTH = 1,6-bis-(2-benzothiazolyldithio)hexane

Table II

	Control Sample 1	Sample 2	Control Sample 3	Control Sample 4	Control Sample 5
Rheometer @ 150°C					
M_{HF} Torque Units (dNm)	40	45	47	38.5	37.5
M_L Torque Units (dNm)	6	5	6	5.5	5.5
M_{HF}-M_L Torque Units (dNm)	34	40	41	33	32
Time to M_{HF} Torque Units, min	20	23	20	20	18.5
Time to 1 PT Rise, min	6	3.5	3.8	6	6
Cure Time, t25, min	8	5	5.2	8.2	8
Cure Time, t90, min	12.5	8	8.2	12.5	12
Reversion (time to drop designated points below maximum torque M_{HF})					
M_{HF} -1 Point	7	97	30	10	12.5
M_{HF} -2 Points	14	none	44	18	31.5
Rheometer @ 170°C					
M_{HF} Torque Units (dNm)	39	45	46	37	36.5
M_L Torque Units (dNm)	5	5	5	5	4.5
M_{HF}-M_L Torque Units (dNm)	34	40	41	32	32
Time to M_{HF} Torque Units, (min)	6	6	6	6	6
t25, (min)	3	2.5	2.5	3	3
t90, (min)	4.2	3.5	3	4.5	4.5
Reversion (time to drop designated points below maximum torque M_{HF})					
M_{HF} -1 Point	1.5	4	4	2	1.5
M_{HF} -2 Points	2.5	9	7	3	3
M_{HF} -3 Points	3.5	14	9	4	4.5
M_{HF} -4 Points	5	25	12	6	6.5
M_{HF} -5 Points	6	64	15	8	13

Table III

	Control Sample 1	Sample 2	Control Sample 3	Control Sample 4	Control Sample 5
Modulus at 300% Elongation, MPa					
20'/150C cure	13.6	15.84	17.02	12.67	11.92
90'/150C cure	9.65	16.2	15.21	11.4	12.19
per cent change	-29	+2.3	-10.6	-10.0	+2.2
6'/170C cure	12.04	14.51	15.56	11.05	10.43
28'/170C cure	6.87	13.36	12.23	8.79	9.77
per cent change	-42.9	-7.9	-21.4	-20.5	-6.3
Tensile Strength, MPa					
20'/150C cure	23.27	19.53	20.32	23.21	21.57
90'/150C cure	18.56	17.98	18.9	20.07	19.39
per cent change	-20.2	-7.9	-7.0	-13.5	-10.1
6'/170C cure	23.37	20.79	20.06	21.35	21.35
28'/170C cure	14.84	18.39	17.93	16.8	17.08
per cent change	-36.4	-11.5	-10.6	-21.3	-20
Elongation at Break, %					
20'/150C cure	479	382	364	498	485
90'/150C cure	491	357	379	474	443
6'/170C cure	514	421	399	504	517
28'/170C cure	514	387	417	484	461

Table III (cont'd)

	Control Sample 1	Sample 2	Control Sample 3	Control Sample 4	Control Sample 5
Shore A Hardness at 100°C					
20'/150C cure	57.4	62.5	63.4	54.9	55.4
90'/150C cure	49.3	61.7	60.9	53	54.6
per cent change	-14.1	-1.3	-3.9	-3.5	-1.4
6'/170C cure	54.3	60.1	61.8	54.1	53.7
28'/170C cure	43	58.8	56.1	48.7	51.4
per cent change	-20.8	-2.2	-9.2	-10.0	-4.4
Percent Rebound at 100°C					
20'/150C cure	71	68.6	70.5	70	68.4
90'/150C cure	63	67.7	68.5	65.1	67
per cent change	-11.3	-1.3	-2.8	-7.0	-2.0
6'/170C cure	69.9	68.8	69.6	68.6	67.6
28'/170C cure	56.1	66.3	66.2	61	63.4
per cent change	-6.9	-3.6	-4.9	-11.1	-6.2

Table III (cont'd)

	Control Sample 1	Sample 2	Control Sample 3	Control Sample 4	Control Sample 5
Heat Rise maximum temp change (°C)					
20'/150°C cure	46	6	10	46	29
55'/150°C cure	38	4	10	41	13
90'/150°C cure	46	2	9	21	16
6'/170°C cure	49	7	13	60	MF
17'/170°C cure	49	4	13	27	13
28'/170°C cure	38	4	10	21	13

MF = machine failure, no value available

Stroke 0.25 inch (6.35 mm) Cyclic Comp 800.00 1/min

Stop Cond Time Sample Failure or 60 min Load on Sample 44.50 lbs (20.18 kg)

Preheat Tmp 93°C Preheat Time 15.00 min

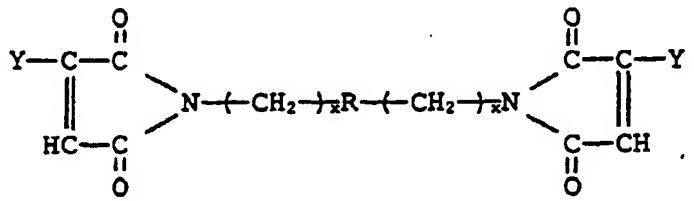
The importance of heat rise is recognized in the article "Internal Temperature Distribution in a Rolling Tire," Tire Science and Technology, Volume 23, No. 1, pages 11-15 (1995) wherein it is stated that sometimes a significant temperature rise in a rolling tire destroys the tire in a short time. Likewise, the article "Heat Generation in Elastomer Compounds: Causes and Effects," Rubber Chemistry and Technology, Volum 64, No. 3, pages 481-492 (1991) dis-

cusses the degradation effects heat rise can have on ultimate physical properties. Accordingly, there is a need in the art for vulcanizates which exhibit low heat rise properties. From the results of Table III, it is clear that the Perkalink® 900/BBDTH combination of the current invention (Sample 2) gave the lowest heat rise to the final vulcanizate versus Controls 1, 3, 4 and 5. This reduction in heat rise thus contributed to the better overall retention of final vulcanizate properties observed.

Claims

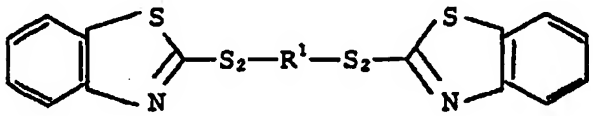
1. A rubber compound having improved reversion resistance characterized by:

(a) a rubber selected from the group consisting of natural rubber, a rubber derived from a diene monomer and mixtures thereof,
(b) from about .1 to about 10 phr of a bismaleimide compound of the general formula:



(I)

wherein R is a divalent acyclic aliphatic group having from about 2 to 16 carbon atoms, cyclic aliphatic group having from about 5 to 20 carbon atoms, aromatic group having from about 6 to 18 carbon atoms, or alkylaromatic group having from about 7 to 24 carbon atoms, wherein these divalent groups may contain a hetero atom selected from O, N and S; X is 0 or an integer of from 1 to 3 and Y is hydrogen or --CH_3; and
(c) from about .1 phr to about 10 phr of a compound of the general formula:



II

where R^1 is selected from the group consisting of alkylene radicals having from 1 to 20 carbon atoms, cycloalkylene radicals having from 6 to 24 carbon atoms and arylene radicals having from 6 to 18 carbon atoms, alkarylene radicals having from 7 to 25 carbon atoms and divalent radicals of the formula:

$$\{R^1\}O\{R^1\}.$$

2. The rubber compound of claim 1 characterized in that said rubber derived from a diene monomer is selected from the group consisting of natural rubber, synthetic cis-1,4-polyisoprene, polybutadiene, polychloroprene, copolymers of isoprene and butadiene, copolymers of acrylonitrile and butadiene, copolymers of acrylonitrile and isoprene, copolymers of styrene, butadiene and isoprene, copolymers of styrene and butadiene and blends thereof.

3. The rubber compound of claim 1 characterized in that said bismaleimide is selected from the group consisting of N,N'-ethylenebismaleimide, N,N'-hexamethylenebismaleimide, N,N'-(m-phenylene)bismaleimide, N,N'-(p-phenylene)bismaleimide, N,N'-(p-tolylene)bismaleimide, N,N'-(methylenedi-p-phenylene)-bismaleimide, N,N'-(oxydi-p-phenylene)bismaleimide, α,α-bis-(4-phenylene)bismaleimide, N,N'-(m-xylylene)bis-citraconimide and α,α-bis-(4-maleimidophenyl)-meta-diisopropylbenzene.

4. The rubber compound of claim 1 characterized in that said compound of formula II is selected from the group consisting of 1,1-bis(2-benzothiazolyldithio)methane; 1,2-bis(2-benzothiazolyldithio)ethane; 1,3-bis(2-benzothiazolyldithio)propane; 1,4-bis(2-benzothiazolyldithio)butane; 1,6-bis(2-benzothiazolyldithio)hexane; 1,8-bis(2-benzothiazolyldithio)octane; 1,10-bis(2-benzothiazolyldithio)decane; 1,10-bis(2-benzothiazolyldithio)octadecane; 1,18-bis(2-benzothiazolyldithio)octadecane; 2,2'-bis(2-benzothiazolyldithio)oxydiethane; 2,2'-bis(2-benzothiazolyldithio)thiodiethane; 4,4'-bis(2-benzothiazolyldithio)oxydibutane; 1,1-bis(2-benzothiazolyldithio)-1,4-cyclohex-

anedimethane; 1,4-bis(2-benzothiazolyldithio)benzene; α,α'-bis(2-benzothiazolyldithio)p-xylene; 1,2-bis(2-benzothiazolyldithio)cyclohexane; 1,1-bis(2-benzothiazolyldithio)cyclohexane; 1,4-bis(2-benzothiazolyldithio)cyclohexane; 1,4-bis(2-benzothiazolyldithio)naphthalene; 4,4'-bis(2-benzothiazolyldithio)biphenyl; 4,4'-bis(2-benzothiazolyldithio)oxybisbenzene and mixtures thereof.

5. The rubber compound of claim 1 characterized in that from 0.5 to 5 phr of the bismaleimide compound is present.

6. The rubber compound of claim 1 characterized in that from 0.5 to 5 phr of the compound of formula II is present.

7. The rubber compound of claim 1 characterized by being in the form of a tire, hose, belt or shoe sole.

8. The rubber compound of claim 7 characterized in that said rubber compound is in the form of a tire.

9. The rubber compound of claim 8 characterized in that said rubber compound is used in a component of said tire selected from the group consisting of wire coat, bead coat, ply coat and tread.

10. The rubber compound of claim 8 characterized in that said tire is selected from the group consisting of a passenger tire, aircraft tire, truck tire, earthmover and agricultural tire.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 11 3303

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	WO 92 07904 A (AKZO NV) * abstract; claims; table 3 * ---	1	C08K5/3415 C08K5/47 C08L21/00
A	CHEMICAL ABSTRACTS, vol. 107, no. 24, 14 December 1987 Columbus, Ohio, US; abstract no. 219005, YAMAZAKI ET AL.: "VULCANIZATION ACCELERATORS FOR RUBBER" XP002046344 * abstract * & JP 62 100 542 A (KAWAGUCHI CHEM. IND.) ---	1	
A	EP 0 564 966 A (GOODYEAR TIRE & RUBBER) * abstract; claims * -----	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C08K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 November 1997	Mettler, R-M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

L1 ANSWER 1 OF 2 CAPLUS COPYRIGHT 2003 ACS
AN 2001:129734 CAPLUS
DN 134:179777
TI Polysulfide vulcanizers and their rubber compositions
IN Maruyama, Tsukasa; Ishikawa, Kazunori
PA Yokohama Rubber Co., Ltd., Japan
SO Jpn. Kokai Tokkyo Koho, 9 pp.
CODEN: JKXXAF
DT Patent
LA Japanese
IC ICM C08L021-00
ICS C08K005-36
CC 39-10 (Synthetic Elastomers and Natural Rubber)
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI JP 2001049046	A2	20010220	JP 1999-225575	19990809 <--
PRAI JP 1999-225575		19990809		

AB Title polysulfides are prepd. by blocking SH-terminated polysulfides HS(YSx)nYSH [Y = (hetero)alkylene; n = 1-00; x = 1.5-3] with unsatd. alicyclic compds., electron-withdrawing group-contg. unsatd. compds., and/or C.gtoreq.4 (hetero)epoxides, followed by addn. reacting with S to an av. bonded S content of >2 and .ltoreq.6. Stirring LP 55 with dicyclopentadiene at 120.degree. for 18 h then with S in presence of Et3N at 90.degree. in vacuo for 16 h gave a product (I), 2.58 parts of which was mixed with Nocceler CZ and a master batch contg. 100 parts isoprene rubber and vulcanized at 148.degree. for 30 min to form a sheet with tensile strength retention 88% and elongation retention 86% after 96 h at 100.degree. and abrasion resistance 15% high than a sheet prepd. from a similar compns. contg. 1.35 phr S instead of the I.

ST modified polysulfide vulcanizer rubber heat resistance; abrasion resistance rubber modified polysulfide vulcanizer

IT Polysulfide rubber
RL: RCT (Reactant); RACT (Reactant or reagent)
(Thiokol LP 55; modified polysulfide vulcanizers for rubber compns. for high abrasion and heat resistance)

IT Heat-resistant materials
(abrasion-resistant; modified polysulfide vulcanizers for rubber compns. for high abrasion and heat resistance)

IT Cycloalkenes
Epoxides
RL: RCT (Reactant); RACT (Reactant or reagent)
(blocking agents for polysulfides; modified polysulfide vulcanizers for rubber compns. for high abrasion and heat resistance)

IT Synthetic rubber, uses
RL: POF (Polymer in formulation); TEM (Technical or engineered material use); USES (Uses)
(diene; modified polysulfide vulcanizers for rubber compns. for high abrasion and heat resistance)

IT Ethers, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(glycidyl, blocking agents for polysulfides; modified polysulfide vulcanizers for rubber compns. for high abrasion and heat resistance)

IT Abrasion-resistant materials
(heat-resistant; modified polysulfide vulcanizers for rubber compns. for high abrasion and heat resistance)

IT Vulcanization accelerators and agents
(modified polysulfide vulcanizers for rubber compns. for high abrasion and heat resistance)

IT Isoprene rubber, uses
RL: POF (Polymer in formulation); TEM (Technical or engineered material use); USES (Uses)
(modified polysulfide vulcanizers for rubber compns. for high abrasion and heat resistance)

IT 121-44-8, Triethylamine, uses
RL: CAT (Catalyst use); USES (Uses)

(in prepn. of modified polysulfides; modified polysulfide vulcanizers for rubber compns. for high abrasion and heat resistance)

IT 9003-31-0
RL: POF (Polymer in formulation); TEM (Technical or engineered material use); USES (Uses)
(isoprene rubber, modified polysulfide vulcanizers for rubber compns. for high abrasion and heat resistance)

IT 77-73-6DP, Dicyclopentadiene, SH-terminated polysulfides blocked with, reaction with sulfur 107-13-1DP, Acrylonitrile, SH-terminated polysulfides blocked with, reaction with sulfur 624-48-6DP, Dimethyl maleate, SH-terminated polysulfides blocked with, reaction with sulfur 2461-15-6DP, 2-Ethylhexyl glycidyl ether, SH-terminated polysulfides blocked with, reaction with sulfur 3101-60-8DP, p-tert-Butylphenyl glycidyl ether, SH-terminated polysulfides blocked with, reaction with sulfur 16245-97-9DP, Stearyl glycidyl ether, SH-terminated polysulfides blocked with, reaction with sulfur
RL: CAT (Catalyst use); IMF (Industrial manufacture); PREP (Preparation); USES (Uses)
(modified polysulfide vulcanizers for rubber compns. for high abrasion and heat resistance)

IT 7704-34-9D, Sulfur, addn. reaction with blocked polysulfides, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(modified polysulfide vulcanizers for rubber compns. for high abrasion and heat resistance)

L1 ANSWER 2 OF 2 CAPLUS COPYRIGHT 2003 ACS
AN 1998:618492 CAPLUS
DN 129:291053
TI Rubber composition containing polysulfides for improved properties and processability
IN Matsui, Tatsuo
PA Toray Thiokol K. K., Japan
SO Jpn. Kokai Tokkyo Koho, 4 pp.
CODEN: JKXXAF
DT Patent
LA Japanese
IC ICM C08L081-04
ICS C08J003-24
CC 39-9 (Synthetic Elastomers and Natural Rubber)
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI JP 10251514	A2	19980922	JP 1997-72635	19970310 <--
PRAI JP 1997-72635		19970310		

AB The compn. comprises 100 parts .gtoreq.1 rubbers derived from crosslinkable elastomers with double bonds and 10-100 parts polysulfides R2SR1(SxR1)nSR2 (x = 2-6 integer; n = 1-50 integer; R1 = C2-10 alkylene and/or oxyalkylene and/or polyoxyalkylene with O no. 2-20: R2 = OH, vinyl, and silyl other than SH). Reaction of polysulfide (LP 3) with ethylene oxide, mixing (75 g) with 22 g S powder and 0.13 g Et3N, kneading (10 parts) with nitrile rubber 90, ZnO 5, dibenzothiazole disulfide 1, and stearic acid 1 part, and vulcanization at 160.degree. for 30 min gave test pieces with JIS A hardness 47, good oil resistance and processability.
ST rubber vulcanization agent polysulfide processability; nitrile rubber polysulfide processability
IT Polysulfides
Polysulfides
RL: MOA (Modifier or additive use); USES (Uses)
(polyoxyalkylene-, vulcanization agents; rubber compn. contg. polysulfides for improved properties and processability)
IT Polyoxyalkylenes, uses
Polyoxyalkylenes, uses
RL: MOA (Modifier or additive use); USES (Uses)
(polysulfide-, vulcanization agents; rubber compn. contg. polysulfides for improved properties and processability)
IT Vulcanization accelerators and agents
(polysulfides; rubber compn. contg. polysulfides for improved properties and processability)
IT Polysulfide rubber
RL: IMF (Industrial manufacture); MOA (Modifier or additive use); PREP (Preparation); USES (Uses)
(reaction product with ethylene oxide, LP 2; rubber compn. contg. polysulfides for improved properties and processability)
IT Polysulfide rubber
RL: IMF (Industrial manufacture); MOA (Modifier or additive use); PREP (Preparation); USES (Uses)
(reaction products, with ethylene oxide; rubber compn. contg. polysulfides for improved properties and processability)
IT Nitrile rubber, properties
Rubber, properties
RL: POF (Polymer in formulation); PRP (Properties); USES (Uses)
(rubber compn. contg. polysulfides for improved properties and processability)
IT 9003-18-3
RL: POF (Polymer in formulation); PRP (Properties); USES (Uses)
(nitrile rubber, rubber compn. contg. polysulfides for improved properties and processability)
IT 75-21-8DP, Ethylene oxide, reaction product with polysulfide
RL: IMF (Industrial manufacture); MOA (Modifier or additive use); PREP (Preparation); USES (Uses)
(rubber compn. contg. polysulfides for improved properties and

processability)

=>

L8 ANSWER 1 OF 11 CAPLUS COPYRIGHT 2003 ACS
AN 2000:137348 CAPLUS
DN 132:167561
TI Manufacture of liquid silylated polysulfides
IN Matsui, Tatsuo; Sakae, Kazuhisa; Iwai, Akira; Saiki, Takeaki
PA Toray Thiokol K. K., Japan; Dow Corning Toray Silicone Co., Ltd.
SO Jpn. Kokai Tokkyo Koho, 8 pp.
CODEN: JKXXAF
DT Patent
LA Japanese
IC ICM C08G075-14
CC 39-10 (Synthetic Elastomers and Natural Rubber)
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2000063521	A2	20000229	JP 1998-230607	19980817
PRAI	JP 1998-230607		19980817		

AB The polysulfides represented by R2(SxR1)nSxR2 (I), useful for rubber vulcanizing agents having rubber-SiO2 binding effect, are manufd. by sulfur exchange reaction of R2SyR2 with R8S(R1Sy)nR1SR8 and/or R8Sy(R1Sy)nR1SyR8 (R1 = C2-10 alkylene, C2-10 oxyalkylene, O2-20 polyoxyalkylene, C3-12 hydroxyalkylene; .gtoreq.1 R2 = R32SiR4R5, R3SiR42R5, R43SiR5, other R2 = C1-20 alkyl, its ester, polyoxyalkylene, PhCH2, C2-18 hydroxyalkyl, hydroxypolyoxyalkylene, R6NR7CS, Me2CHOCS, C6H4SNC, OC4H8N; R8 = R2 in R2SxR2; x > 2 and .ltoreq. 6; y .gtoreq. 2; n = 1-100; R3 = C1-4 alkyl; R4 = C1-8 alkoxy; R5 = C2-12 alkylene, its ester, amide, ether; R6, R7 = Me, Et, Bu, C5H10, PhCH2). Thus, **Thiokol** LP 3 (mol. wt. 1000) was treated with 1.4 mol/mol-SH ethylene oxide, further treated with 3-isocyanatopropyltriethoxysilane in presence of an amine catalyst, further treated with S, and then 40 g of the product was treated with 10 g bis(3-triethoxysilylpropyl)tetrasulfide in presence of Et3N to give I (n .apprx.3, x = 4).

ST silylated polysulfide prepn rubber vulcanizer; silica rubber binder silylated polysulfide prepn

IT Polysulfide rubber
RL: IMF (Industrial manufacture); MOA (Modifier or additive use); PREP (Preparation); USES (Uses)
(ethoxylated, silylated; manuf. of liq. silylated polysulfides for rubber vulcanizers having rubber-silica binding effect)

IT Binders
Vulcanization accelerators and agents
(manuf. of liq. silylated polysulfides for rubber vulcanizers having rubber-silica binding effect)

IT Polysulfides
RL: IMF (Industrial manufacture); MOA (Modifier or additive use); PREP (Preparation); USES (Uses)
(silylated; manuf. of liq. silylated polysulfides for rubber vulcanizers having rubber-silica binding effect)

IT 75-21-8DP, Ethylene oxide, reaction products with polysulfides, isocyanatopropyltriethoxysilane, sulfur, and bis(triethoxysilylpropyl) tetrasulfide 103-34-4DP, reaction products with polysulfides **120-78-5DP**, Dibenzothiazyl disulfide, reaction products with polysulfides 137-26-8DP, Tetramethylthiuram disulfide, reaction products with polysulfides 4420-74-0DP, .gamma.-Mercaptopropyltrimethoxysilane, reaction products with polysulfides 7704-34-9DP, Sulfur, reaction products with silylated polysulfides and bis(triethoxysilylpropyl) tetrasulfide, preparation 24801-88-5DP, 3-Isocyanatopropyltriethoxysilane, reaction products with ethoxylated polysulfides, sulfur, and bis(triethoxysilylpropyl) tetrasulfide 40372-72-3DP, Bis(3-triethoxysilylpropyl) tetrasulfide, reaction products with polysulfides 195460-35-6DP, **Thiokol** LP 23, reaction products with sulfur and alkoxy silanes
RL: IMF (Industrial manufacture); MOA (Modifier or additive use); PREP (Preparation); USES (Uses)
(manuf. of liq. silylated polysulfides for rubber vulcanizers having rubber-silica binding effect)

L8 ANSWER 2 OF 11 CAPLUS COPYRIGHT 2003 ACS
AN 1999:753279 CAPLUS
DN 131:352483
TI Polysulfide polymers and process for their manufacture
IN Matsui, Tatsuro; Sakae, Kazuhisa
PA Toray Thiokol Co., Ltd., Japan
SO PCT Int. Appl., 25 pp.
CODEN: PIXXD2
DT Patent
LA Japanese
IC ICM C08G075-14
CC 39-10 (Synthetic Elastomers and Natural Rubber)
Section cross-reference(s): 35
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 9960047	A1	19991125	WO 1999-JP2581	19990518
	W: US				
	RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
	JP 11322931	A2	19991126	JP 1998-153591	19980518
PRAI	JP 1998-153591		19980518		

AB The polymers are of R(SxZ1)nSxR type compds. (Z = C2-10 alkylene, oxyalkyene, O2-20 polyoxyalkylene, C3-12 hydroxyalkylene group; x = 2-6; n = 2-100; R = specific functional groups), which are useful as vulcanizing agents for rubbers having double bonds, and have terminal groups effective in accelerating the vulcanization of rubbers, e.g., benzothiazolyl or thiocarbamyl, and alkyl groups effective in enhancing the compatibility with mineral oils, or other necessary chem. structures. Thus, prepg. an ethylene oxide adduct of **Thiokol** LP 23, i.e., HS(CH2CH2OCH2OCH2CH2S2)12CH2CH2OCH2OCH2CH2SH (at ethylene oxide/SH equiv. ratio 1.5:1), mixing (91 g) with dibenzothiazyl disulfide 26, powd. S 33, Et3N 0.4 and PhMe 45 g at 80.degree. for 1 h under N gave a modified polysulfide (I). Kneading natural rubber 94 with the I 6, ZnO 5 and stearic acid 2 parts at 150.degree. gave a vulcanized product without the needs for addnl. vulcanization agent.

ST polysulfide polymer vulcanization agent rubber; natural rubber vulcanization agent polysulfide polymer

IT Polysulfide rubber
RL: IMF (Industrial manufacture); MOA (Modifier or additive use); PREP (Preparation); USES (Uses)
(alkoxylated and functionally modified; vulcanization agent; manuf. of functional group-terminated polysulfide polymers for rubber vulcanization)

IT Vulcanization accelerators and agents
(manuf. of functional group-terminated polysulfide polymers for rubber vulcanization)

IT Natural rubber, uses
Nitrile rubber, uses
RL: PEP (Physical, engineering or chemical process); POF (Polymer in formulation); PROC (Process); USES (Uses)
(manuf. of functional group-terminated polysulfide polymers for rubber vulcanization)

IT Polysulfides
RL: IMF (Industrial manufacture); MOA (Modifier or additive use); PREP (Preparation); USES (Uses)
(vulcanization agents; manuf. of functional group-terminated polysulfide polymers for rubber vulcanization)

IT 9003-18-3
RL: PEP (Physical, engineering or chemical process); POF (Polymer in formulation); PROC (Process); USES (Uses)
(nitrile rubber, manuf. of functional group-terminated polysulfide polymers for rubber vulcanization)

IT 75-18-3DP, Dimethyl sulfide, reaction products with polysulfides and other modifiers 75-21-8DP, Ethylene oxide, reaction products with polysulfides and rubber-vulcanizable compds. **120-78-5DP,**

Dibenzothiazyldisulfide, reaction products with polysulfides and other modifiers 137-26-8DP, Tetramethylthiuram disulfide, reaction products with polysulfides and other modifiers 7704-34-9DP, Sulfur, reaction products with alkoxylated polysulfides and rubber-vulcanizable compds., preparation 25103-58-6DP, tert-Dodecyl mercaptan, reaction products with polysulfides and other modifiers 195460-35-6DP, **Thiokol** LP 23, alkoxylated and functionally modified
RL: IMF (Industrial manufacture); MOA (Modifier or additive use); PREP (Preparation); USES (Uses)
(vulcanization agent; manuf. of functional group-terminated polysulfide polymers for rubber vulcanization)

RE.CNT 10 THERE ARE 10 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

(1) Nippon Shokubai Co Ltd; FR 2748750 A1 CAPLUS
(2) Nippon Shokubai Co Ltd; JP 10-67853 A 1998 CAPLUS
(3) Saiokooru Chemical Corp; GB 1071826 A CAPLUS
(4) Saiokooru Chemical Corp; CA 822132 A
(5) Saiokooru Chemical Corp; JP 41-19514 B1 1966
(6) Toray Thiokol Co Ltd; EP 424143 A2 CAPLUS
(7) Toray Thiokol Co Ltd; US 5393861 A CAPLUS
(8) Toray Thiokol Co Ltd; JP 04-363325 A 1992 CAPLUS
(9) Toray Thiokol Co Ltd; JP 04-7331 A 1992 CAPLUS
(10) Toray Thiokol Co Ltd; JP 10-120788 A 1998 CAPLUS

L8 ANSWER 3 OF 11 CAPLUS COPYRIGHT 2003 ACS

AN 1997:303021 CAPLUS
DN 126:278781

TI Curable polysulfide compositions giving heat-resistant white rubbers for sealants

IN Matsui, Tatsuro
PA Toray Thiokol Kk, Japan

SO Jpn. Kokai Tokkyo Koho, 4 pp.
CODEN: JKXXAF
DT Patent
LA Japanese
IC ICM C08L081-04
ICS C08K003-22; C08K005-31; C08K005-36; C08K005-56
CC 39-10 (Synthetic Elastomers and Natural Rubber)
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 09059515	A2	19970304	JP 1995-239177	19950824
PRAI	JP 1995-239177		19950824		

AB Title compns. contain polysulfides having .gtoreq.2 SH groups and Zn phyllosilicate and/or Al Zn phyllosilicate as curing agent(s). Thus, LP 55 (SH-contg. polysulfides) was mixed with 20% Mizukanite (5ZnO.Al2O3.3SiO2.5H2O/4SiO2) at room temp. to give a white cured product within 1 day.

ST thiol contg polysulfide crosslinker zinc phyllosilicate; aluminum zinc phyllosilicate crosslinker polysulfide rubber; heat resistant white polysulfide rubber crosslinker; sealing polysulfide rubber white crosslinker phyllosilicate

IT Polysulfide rubber
RL: PEP (Physical, engineering or chemical process); POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); PROC (Process); USES (Uses)
(**Thiokol** LP 55; polysulfide compns. contg. phyllosilicates as curing agents for heat-resistant white sealing rubbers)

IT Sealing compositions
Sealing compositions
(heat-resistant; polysulfide compns. contg. phyllosilicates as curing agents for heat-resistant white sealing rubbers)

IT Silicates, uses
RL: CAT (Catalyst use); USES (Uses)
(phyllo-, vulcanization catalysts; polysulfide compns. contg. phyllosilicates as curing agents for heat-resistant white sealing rubbers)

IT Vulcanization accelerators and agents
(phyllosilicates; in polysulfide compns. for heat-resistant white sealing rubbers)
IT Heat-resistant materials
Heat-resistant materials
(sealants; polysulfide compns. contg. phyllosilicates as curing agents for heat-resistant white sealing rubbers)
IT 52488-90-1, Aluminum zinc silicate
RL: CAT (Catalyst use); USES (Uses)
(Mizukanite, crosslinking catalysts; polysulfide compns. contg. phyllosilicates as curing agents for heat-resistant white sealing rubbers)
IT 11126-29-7, Zinc silicate
RL: CAT (Catalyst use); USES (Uses)
(crosslinking catalysts; polysulfide compns. contg. phyllosilicates as curing agents for heat-resistant white sealing rubbers)
IT 7704-34-9, Sulfur, uses
RL: MOA (Modifier or additive use); USES (Uses)
(polysulfide compns. contg. phyllosilicates as curing agents for heat-resistant white sealing rubbers)
IT 77-58-7 78-04-6, Dibutyltin maleate 105833-70-3, Octenoic acid lead salt
RL: CAT (Catalyst use); USES (Uses)
(vulcanization accelerator; polysulfide compns. contg. phyllosilicates as curing agents for heat-resistant white sealing rubbers)
IT **120-78-5**, Dibenzylthiazyl disulfide
RL: MOA (Modifier or additive use); USES (Uses)
(vulcanization accelerator; polysulfide compns. contg. phyllosilicates as curing agents for heat-resistant white sealing rubbers)

L8 ANSWER 4 OF 11 CAPLUS COPYRIGHT 2003 ACS
AN 1994:517353 CAPLUS
DN 121:117353
TI Depilatory compositions containing liquid polysulfide and metal oxides
IN Futami, Shunichi
PA GC Corp., Japan
SO Fr. Demande, 16 pp.
CODEN: FRXXBL
DT Patent
LA French
IC ICM A61K007-155
CC 62-4 (Essential Oils and Cosmetics)
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	FR 2691628	A1	19931203	FR 1993-6402	19930528
	FR 2691628	B1	19941209		
PRAI	JP 1992-134394		19920601		

AB Depilatory compns. contg. liq. polysulfide (av. mol. wt. = 1000-7500) and metal oxides are claimed. Equal vols. of paste A contg. **Thiokol** LP-3 (a polysulfide polymer) 58, CaCO3 20, CaSO4 10, BaSO4 10, dioctyl sebacate 2, S 0.2% and paste B contg. PbO2 45, tetra-Bu thiuram sulfide 2, TiO2 28, di-Et phthalate 3, chlorinated paraffins 20, Bu oleate 2% were mixed for 60 s to obtain a compn. having hardening time of 12 min.
ST depilatory compn liq polysulfide metal oxide; **Thiokol** LP3
titanium oxide cosmetic depilatory; lead oxide **Thiokol** LP3
cosmetic depilatory
IT Oxides, biological studies
Peroxides, biological studies
RL: BIOL (Biological study)
(depilatory compns. contg. liq. polysulfide and)
IT Vulcanization accelerators and agents
Olive oil
RL: BIOL (Biological study)
(depilatory compns. contg. liq. polysulfide and metal oxides and)
IT Rubber, polysulfide
RL: BIOL (Biological study)

(depilatory compns. contg. metal oxides and)
IT Paraffin oils
RL: BIOL (Biological study)
(chloro, depilatory compns. contg. liq. polysulfide and metal oxides and)
IT Cosmetics
(depilatories, liq. polysulfide and metal oxides in)
IT Cosmetics
(depilatories, creams, liq. polysulfide and metal oxides in)
IT Fatty acids, uses
RL: BIOL (Biological study)
(esters, depilatory compns. contg. liq. polysulfide and metal oxides and)
IT Polymers, biological studies
RL: BIOL (Biological study)
(sulfur-contg., liq., depilatory compns. contg. metal oxides and)
IT Fats and Glyceridic oils
RL: BIOL (Biological study)
(vegetable, depilatory compns. contg. liq. polysulfide and metal oxides and)
IT 137-26-8, Tetramethyl thiuram disulfide 1305-79-9, Calcium peroxide 1309-60-0, Lead oxide 1309-64-4, Antimony trioxide, biological studies 1314-22-3, Zinc peroxide 14452-57-4, Magnesium peroxide 101395-74-8, Manganese peroxide
RL: BIOL (Biological study)
(depilatory compns. contg. liq. polysulfide and)
IT 84-66-2, Diethyl phthalate 84-69-5, Isobutyl phthalate 84-74-2, Dibutyl phthalate 97-74-5, Tetramethylthiuram monosulfide 97-77-8, Tetraethyl thiuram disulfide 103-23-1, Dioctyl adipate 109-43-3, Dibutyl sebacate 117-81-7, Dioctyl phthalate 120-54-7, Dipentamethylene thiuram tetrasulfide **120-78-5** 123-95-5, Butyl stearate 131-11-3 136-23-2, Zinc dibutyl dithiocarbamate 137-30-4, Zinc dimethyl dithiocarbamate 149-30-4, 2-Mercaptobenzothiazole 471-34-1, Calcium carbonate, biological studies 1314-13-2, Zinc oxide, biological studies 1634-02-2, Tetrabutyl thiuram disulfide 2064-80-4, Dioctyl azelate 2432-87-3, Dioctyl sebacate 7631-86-9, Silica, biological studies 7727-43-7, Barium sulfate 7778-18-9, Calcium sulfate 11092-32-3, Aluminum dioxide 13037-20-2, Ethyl phenyl dithiocarbamate 13463-67-7, Titanium dioxide, biological studies 14324-55-1, Zinc diethyl dithiocarbamate
RL: BIOL (Biological study)
(depilatory compns. contg. liq. polysulfide and metal oxides and)

L8 ANSWER 5 OF 11 CAPLUS COPYRIGHT 2003 ACS
AN 1994:253062 CAPLUS
DN 120:253062
TI Polysulfide polymers as depilating agents
IN Futami, Shunichi
PA GC Corp., Japan
SO Ger. Offen., 8 pp.
CODEN: GWXXBX
DT Patent
LA German
IC ICM A61K007-155
CC 62-3 (Essential Oils and Cosmetics)
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 4317988	A1	19931202	DE 1993-4317988	19930528
	JP 06048927	A2	19940222	JP 1993-142527	19930524
	JP 2798584	B2	19980917		
	US 5417966	A	19950523	US 1993-65999	19930524
	GB 2267436	A1	19931208	GB 1993-10821	19930526
	GB 2267436	B2	19960522		
PRAI	JP 1992-163394		19920601		

AB A depilatory for human use comprises paste A contg. liq. polysulfide polymer (mean mol. wt. 1000-7500) 55-85, liq. component 1-10, and filler

10-40 wt.% and paste B contg. metal oxide or peroxide 30-60, vulcanization accelerator 2-10, filler 2-30, and liq. component 20-50 wt.%. On mixing the pastes and applying to the skin, the polysulfide polymer penetrates into the hair, binds to keratin, and hardens to a rubbery state, which facilitates removal of the hair from the roots painlessly or with very little pain. Thus, paste A contained Thiocol LP-2 70, powd. SiO_2 10, powd. Al_2O_3 15, di-Bu phthalate 3, dioctyl azelate 2, and powd. S 0.5 wt.%, and paste B contained ZnO_2 12, Sb_2O_3 20, tetramethylthiuram disulfide 4, Zn ethylphenyldithiocarbamate 3, powd. SiO_2 16, chlorinated paraffin 35, and Bu stearate 10 wt.%. The pastes were mixed for 60 s; the hardening time was 10 min.

ST polysulfide depilatory

IT Polysulfides
RL: BIOL (Biological study)
(depilatories contg.)

IT Rubber, polysulfide
RL: BIOL (Biological study)
(depilatories contg. **Thiokol** LP)

IT Vulcanization accelerators and agents
Oxides, biological studies
Peroxides, biological studies
RL: BIOL (Biological study)
(depilatories contg. polysulfides and)

IT Cosmetics
(depilatories, polysulfide polymers in)

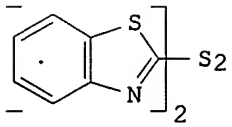
IT 97-74-5, Tetramethylthiuram monosulfide 97-77-8, Tetraethylthiuram disulfide 120-54-7, Dipentamethylenethiuram tetrasulfide **120-78-5**, 2-Benzothiazyl disulfide 136-23-2, Zinc dibutyldithiocarbamate 137-26-8, Tetramethylthiuram disulfide 137-30-4, Zinc dimethyldithiocarbamate 149-30-4, 2-Mercaptobenzothiazole 1305-79-9, Calcium peroxide 1309-60-0, Lead peroxide 1309-64-4, Antimony trioxide, biological studies 1313-13-9, Manganese dioxide, biological studies 1314-13-2, Zinc oxide (ZnO), miscellaneous 1314-22-3, Zinc peroxide 1634-02-2, Tetrabutylthiuram disulfide 7704-34-9, Sulfur, miscellaneous 14324-55-1, Zinc diethyldithiocarbamate 14452-57-4, Magnesium peroxide 14634-93-6, Zinc ethylphenyldithiocarbamate
RL: BIOL (Biological study)
(depilatories contg. polysulfides and)

L8 ANSWER 6 OF 11 CAPLUS COPYRIGHT 2003 ACS
AN 1983:22315 CAPLUS
DN 98:22315
TI Catalyst compositions for curing polythiopolymercaptan polymers
IN Larson, Melvin L.
PA Sybron Corp., USA
SO Eur. Pat. Appl., 14 pp.
CODEN: EPXXDW
DT Patent
LA English
IC C08L081-04; B01J031-26; A61K006-10
CC 63-7 (Pharmaceuticals)

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	EP 61242	A1	19820929	EP 1982-301047	19820302
	R: AT, BE, CH, DE, FR, GB, IT, NL, SE				
	US 4362649	A	19821207	US 1981-247231	19810325
	CA 1160617	A1	19840117	CA 1982-396824	19820223
	AU 8280964	A1	19820930	AU 1982-80964	19820301
	BR 8201637	A	19830216	BR 1982-1637	19820324
	JP 57169411	A2	19821019	JP 1982-46458	19820325
PRAI	US 1981-247231		19810325		

GI



I

AB A catalyst compn. for mouth temp. curing of liq. polythiopolymercaptan polymers to produce elastomeric dental impression materials comprises acid-treated submicron ZnO (the acid preferably being EtCO2H [79-09-4]) and purified benzothiazolyl disulfide (I) [**120-78-5**]. A compn. contg. **Thiokol** LP-2 in base paste 100.00 and catalyst paste contg. ZnO 82.38, I 13.56, di-Bu phthalate 39.15, TiO2 32.88, and pigment 1.53 parts by wt., worked 3-4 min, and cured at 32.degree. for 6 min gave a compression set of 1.4% and strain in compression 9.1%. Two wk later the room-temp. rubber specimens had strain in compression of 9.8%.

ST polysulfide rubber dental impression catalyst; benzothiazole disulfide catalyst polysulfide rubber

IT Vulcanization accelerators
(acid-treated zinc oxide and benzothiazolyl disulfide, for polysulfide rubber dental impression compns.)

IT Rubber, polysulfide
RL: BIOL (Biological study)
(for dental impressions, catalyst compn. for curing)

IT Dental materials and fillings
(impressions, polysulfide rubber, crosslinking compns. for)

IT 1314-13-2, biological studies
RL: BIOL (Biological study)
(acid-treated, crosslinking compn. contg., for polysulfide rubber dental impressions)

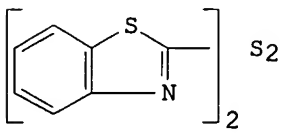
IT **120-78-5**
RL: CAT (Catalyst use); USES (Uses)
(crosslinking catalyst contg., for polysulfide rubber dental impressions)

IT 79-09-4, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(zinc oxide treated with, for crosslinking catalysts, for polysulfide rubber dental impression compns.)

L8 ANSWER 7 OF 11 CAPLUS COPYRIGHT 2003 ACS
AN 1978:465282 CAPLUS
DN 89:65282
TI Cure material for liquid polythiopolymercaptan polymers for dental impression taking
IN Kessler, Henry A.; Ying, Phyllis
PA Warner-Lambert Co., USA
SO U.S., 3 pp.
CODEN: USXXAM
DT Patent
LA English
IC B01J031-26
NCL 252430000
CC 63-7 (Pharmaceuticals)
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 4082693	A	19780404	US 1976-739410	19761108
PRAI	US 1976-739410		19761108		

GI



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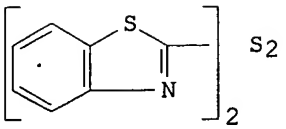

I

AB Liq. polysulfides are treated with a synergistic accelator system comprising peroxide 20-75, 2,2'-dithiobisbenzothiazole (I) [**120-78-5**] 5-30, 2-mercaptobenzothiazole (II) [149-30-4] 0.05-20%, and fillers, to obtain an improved pastelike dental elastomeric impression material. The 2 components, accelerator system (A) and liq. polysulfide (B) are in a 1:1 ratio. Thus, A was prepd. by blending at room temp. I contg. 1.33% II 10.29, purified II .apprx.0.67 (adjusted to give a final 2%), 2-ethylhexyl diphenyl phosphate 22.80, Et oleate 7.42, color 0.32, Zn peroxide 47.72, SiO2 0.65, and ZnO to make 100 g. The resulting paste was packaged in Al tubes. B comprised SiO2 colloidal 0.95, LP-2 **Thiokol** 75.72, clove oil 0.14, ZnS 17.04, Mg trisilicate 6.15 g.

ST polysulfide rubber dental impression accelerator; dental elastic impression polysulfide; benzothiazole cure material dental polysulfide

IT Rubber, polysulfide
RL: BIOL (Biological study)
(dental impression material, zinc peroxide and dithiobenzothiazole accelerator assistance for)

IT Dental materials and fillings
(for impressions, polysulfide rubber, dithiobisbenzothiazole and zinc peroxide curing agents for)

IT **120-78-5** 149-30-4 1314-22-3
RL: BIOL (Biological study)
(curing agent contg., for polysulfide rubber dental impression material)

L8 ANSWER 8 OF 11 CAPLUS COPYRIGHT 2003 ACS
AN 1977:18095 CAPLUS
DN 86:18095
TI Vulcanization accelerators for polysulfide rubber
IN Braden, Michael
PA London Hospital Medical College, UK
SO Ger. Offen., 12 pp.
CODEN: GWXXBX
DT Patent
LA German
IC C08L081-04
CC 38-10 (Elastomers, Including Natural Rubber)
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 2610685	A1	19760930	DE 1976-2610685	19760313
	GB 1547372	A	19790613	GB 1975-11057	19750317
	ZA 7601351	A	19770223	ZA 1976-1351	19760305
	CA 1072071	A1	19800219	CA 1976-247433	19760309
	FR 2304641	A1	19761015	FR 1976-6915	19760311
	FR 2304641	B1	19810320		
	AU 7611874	A1	19770929	AU 1976-11874	19760311
	SE 7603239	A	19760918	SE 1976-3239	19760312
	NL 7602633	A	19760921	NL 1976-2633	19760312
	NO 7600899	A	19760920	NO 1976-899	19760315
	NO 148675	B	19830815		
	NO 148675	C	19831123		
	DK 7601121	A	19760918	DK 1976-1121	19760316
	CH 630104	A	19820528	CH 1976-3245	19760316
	BE 839668	A1	19760716	BE 1976-165256	19760317
	JP 51145485	A2	19761214	JP 1976-29075	19760317
	NO 7900128	A	19760920	NO 1979-128	19790115
PRAI	GB 1975-11057		19750317		
	GB 1975-12533		19750325		

AB Polysulfide rubber is cured relatively rapidly at room temp. in the presence of $ZnCO_3$, disulfide accelerators, and S-amine complexes which prevent undesired softening of the cured rubber. Thus, combining 7 parts mixt. of **Thiokol** LP2 300, 30% lithopone 443, plasticizer (Santicizer B16) (I) 105, TiO_2 7, Aerosil-130 17, and cobalt blue pigment 28 parts with 2 parts mixt. of $ZnCO_3$ [3486-35-9] 373, Vulcafor MBTS (bisbenzothiazol-2-yl disulfide) [**120-78-5**] 269, I 524, and 9:1 rhomboidal S-Et_2NH [109-89-7] complex 5.65 parts gives a compn. which cures in 10 min at room temp. to IRH hardness 28-60.

ST vulcanization accelerator polysulfide rubber; zinc carbonate vulcanization polysulfide; benzothiazole disulfide vulcanization polysulfide

IT Rubber, polysulfide
RL: USES (Uses)
(vulcanization accelerators for, zinc carbonate-benzothiazyldisulfide as)

IT Vulcanization accelerators
(zinc carbonate-benzothiazyldisulfide, for polysulfide rubber at room temp.)

IT 109-89-7D, complexes with sulfur 7704-34-9D, complexes with amines
RL: PROC (Process)
(polysulfide rubber vulcanization in presence of, for softening prevention)

IT **120-78-5** 3486-35-9
RL: USES (Uses)
(vulcanization accelerators, for polysulfide rubber at room temp.)

L8 ANSWER 9 OF 11 CAPLUS COPYRIGHT 2003 ACS
AN 1976:594288 CAPLUS
DN 85:194288
TI Single-package, polysulfide-type sealants hardenable by moisture
IN Price, Norman Owen; Coates, Harold; Scott, Christopher
PA Albright and Wilson Ltd., UK
SO Ger. Offen., 53 pp.
CODEN: GWXXBX
DT Patent
LA German
IC C09K003-10
CC 42-11 (Coatings, Inks, and Related Products)
Section cross-reference(s): 38

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 2611802	A1	19761007	DE 1976-2611802	19760319
	SE 7603407	A	19760922	SE 1976-3407	19760318
	FR 2304649	A1	19761015	FR 1976-8139	19760319
	FR 2304649	B1	19790720		
	GB 1547171	A	19790425	GB 1975-11862	19760319
	JP 51119061	A2	19761019	JP 1976-30010	19760322
PRAI	GB 1975-11862		19750321		
	GB 1975-11863		19750321		
	GB 1975-11864		19750321		

AB The title sealants, extrudable and elastomeric, contain polysulfides, 3-30% of the SH groups of which are reacted with SH-reactive, hydrolyzable silanes, and carbamoyl, thiocarbamoyl, or imidocarbamoyl disulfides. Thus, refluxing polysuflide (**Thiokol** LP 12) 500, S 5, $CH_2{:}CHSi(OMe)_2Me$ [16753-62-1] 15, and PhMe 500 g 15 hr gives a product with 23.9% SH groups reacted. This soln. (75 g) is stripped of PhMe, 25 g residue is combined with 0.50 g tetramethylthiuran disulfide [137-26-8], 0.50 g $(Me_2CH)_2Ti(acetylacetonato)_2$, and 25 g filler (14.0 g chlorinated paraffin, 4.0 g Ti oxide, 17.5 g $CaCO_3$) and cured 7 days at room temp. and 50% relative humidity to give a product with 75% modulus 6.35 kg, elongation to cohesive failure 90%, and instant elastic recovery 90%.

ST polysulfide rubber sealant; vinylsilane polysuflide sealant; thiuran disulfide polysulfide sealant; silane vinyl polysulfide sealant; disulfide carbamoyl polysulfide sealant

IT Vulcanization accelerators
(neg., silanes and ortho esters as, for moisture-curable polysulfide

rubber sealants)
IT Vulcanization
(of silane-modified polysulfide rubber sealants, by moisture)
IT Sealing compositions
(silane-modified polysuflide rubber, moisture-curable)
IT Rubber, polysulfide
(silane-modified, sealants, moisture-curable)
IT Silane, ethenyldimethoxymethyl-, reaction products with polysulfides
RL: USES (Uses)
(sealants, moisture-curable)
IT 103-34-4 **120-78-5** 137-26-8 502-55-6 1634-02-2 10591-84-1
RL: USES (Uses)
(polysulfide rubber sealants contg., moisture-curable)
IT 78-39-7 115-80-0 1185-55-3
RL: USES (Uses)
(vulcanization inhibitors, for polysulfide rubber sealants)

L8 ANSWER 10 OF 11 CAPLUS COPYRIGHT 2003 ACS
AN 1976:91400 CAPLUS
DN 84:91400
TI Curing of liquid polythiopolymercaptan polymers
IN Pellico, Michael A.
PA Denton Industries, Inc., USA
SO U.S., 6 pp.
CODEN: USXXAM
DT Patent
LA English
IC C08G
NCL 260079000
CC 38-13 (Elastomers, Including Natural Rubber)
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 3923754	A	19751202	US 1974-518378	19741029
PRAI	US 1973-414893		19731112		

AB Liq. polythiopolymercaptan rubbers were room-temp. vulcanized in 15 min using .gtoreq.20 parts polysulfide and .gtoreq.20 parts of zinc component. Thus, liq. polysulfide rubber (**Thiokol** LP 2), blended at room temp. with 20 parts zinc oxide (I) [1314-13-2] and 20 parts tetramethylthiuram disulfide [137-26-8] had working life 5 min and cure time 9 min, compared with 15.5 and 25, resp., for a similar compn. contg. 5 parts I.
ST liq polysulfide rubber vulcanization; zinc oxide vulcanization polysulfide; thiuram vulcanization liq polysulfide
IT Vulcanization accelerators
(thiuram disulfides-zinc oxides, for polysulfide rubber)
IT Rubber, polysulfide
(vulcanization accelerators for, thiuram disulfides-zinc oxides as)
IT 1314-13-2, uses and miscellaneous 1314-22-3
RL: USES (Uses)
(vulcanization accelerators, contg. thiuram disulfides, for polysulfide rubbers)
IT 97-77-8 **120-78-5** 137-26-8 971-15-3 1634-02-2
RL: USES (Uses)
(vulcanization accelerators, contg. zinc oxides, for polysulfide rubber)

L8 ANSWER 11 OF 11 CAPLUS COPYRIGHT 2003 ACS
AN 1969:413784 CAPLUS
DN 71:13784
TI Liquid polymers containing mercaptan groups and modified by thiazoles
IN Millen, Edward G.; Koons, Paul A.
PA Thiokol Chemical Corp.
SO Fr., 7 pp.
CODEN: FRXXAK
DT Patent
LA French

IC C08K
CC 36 (Plastics Manufacture and Processing)
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	FR 1546113		19681115		
PRAI	US		19661213		

AB Liq. polymers contg. SH groups were hardened with .gtoreq.1 hardening and oxidizing agent and a co-hardening agent selected from thiazoles and thiazolines. The liq. polymers are useful in caulking compns., esp. in the construction and automobile industry, for molding, impregnation of leather and textiles, adhesives, and coatings. Thus, a mixt. of 25 parts LP-31 [HS(CH2CH2OCH2OC2H4SS)42CH2CH2OCH2OC2H4SH] and 1.5 parts ZnO2 was hardened with 1 part 2-mercaptothiazoline. The compn. reached Shore hardness .apprx.25 in 2 hrs. at 82.degree.. When ZnO2 was used alone as the hardening agent, in 7 hrs. at 82.degree. the Shore hardness was <25.degree.. Other hardening and oxidizing agents used were BaMnO4, Li2O2, KIO3, (NH4)2Cr2O7, CaO2, MnO2, and TeO2. Other co-hardening agents used were 1,3 - bis(2 - benzothiazolylmercaptomethyl)urea, 2-mercaptoben-zothiazole, benzothiazolyl disulfide, N-(oxydiethylene)benzothiazole - 2-sulfenamide, N-cyclohexylbenzothiazole - 2-sulfenamide, and N,N-diisopropylbenzothiazole - 2-sulfenamide. Other liq. polymers used were LP-32 [HS(CH2CH2OCH2OCH2CH2SS)23CH2CH2OCH2OCH2CH2SH], an acrylonitrile-butadiene copolymer with terminal SH groups, and polypropylene glycol with terminal SH groups.

ST polyethylene oxides sulfides hardening

IT Rubber, nitrile, reactions
(mercapto-terminated, vulcanization of, by oxidizing agents and thiazoles)

IT Crosslinking
(of **Thiokol** rubber, by oxidizing agents and thiazoles)

IT Rubber, **Thiokol**
(vulcanization of, by oxidizing agents and thiazoles)

IT 102-77-2
RL: RCT (Reactant); RACT (Reactant or reagent)
(vulcanization of **Thiokol** rubber by)

IT 95-29-4 95-33-0 95-35-2 **120-78-5** 149-30-4 5459-03-0
RL: USES (Uses)
(vulcanization of **Thiokol** rubber by oxidizing agents and)

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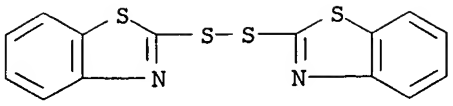
L5 ANSWER 4 OF 4 REGISTRY COPYRIGHT 2003 ACS
RN 120-78-5 REGISTRY
CN Benzothiazole, 2,2'-dithiobis- (8CI, 9CI) (CA INDEX NAME)
OTHER NAMES:
CN 2,2'-Benzothiazolyl disulfide
CN 2,2'-Benzothiazyl disulfide
CN 2,2'-Dibenzothiazole disulfide
CN 2,2'-Dibenzothiazolyl disulfide
CN 2,2'-Dithiobis[benzothiazole]
CN 2-Benzothiazolyl disulfide
CN 2-Benzothiazyl disulfide
CN 2-Mercaptobenzothiazole disulfide
CN Accel DM
CN Accel TM
CN Altax
CN Benzothiazole disulfide
CN Benzothiazolyl disulfide
CN Benzothiazyl disulfide
CN Bis(2-benzothiazole) 2,2'-disulfide
CN Bis(2-benzothiazolyl) 2,2'-disulfide
CN Bis(2-benzothiazolyl) disulfide
CN Bis(2-benzothiazyl) disulfide
CN DBTD
CN Di-2-benzothiazolyl disulfide
CN Dibenzothiazolyl disulfide
CN Dibenzothiazyl disulfide
CN Dibenzthiazyl disulfide
CN DM
CN DM (accelerator)
CN Ekagom GS
CN **MBTS**
CN **MBTS rubber accelerator**
CN **Merasulf MBTS**
CN Nocceler DM
CN Nocceler DM-PO
CN NSC 677459
CN **Perkacit MBTS**
CN Pneumax DM
CN **Royal MBTS**
CN Sanceler DM
CN Soxinol DM
CN Thiofide
CN **Thiofide MBTS**
CN Tiazol 2MBS
CN **Vulcafor MBTS**
CN Vulkacit DM
CN Vulkacit DM/C
CN Vulkacit DM/MG
CN Vulkafil ZN 96TT11
CN Wobezit DM
FS 3D CONCORD
DR 109767-80-8, 137497-18-8
MF C14 H8 N2 S4
CI COM
LC STN Files: AQUIRE, BEILSTEIN*, BIOBUSINESS, BIOSIS, BIOTECHNO, CA, CANCERLIT, CAOLD, CAPLUS, CASREACT, CHEMCATS, CHEMINFORMRX, CHEMLIST, CIN, CSCHEM, CSNB, EMBASE, HSDB*, IFICDB, IFIPAT, IFIUDB, MEDLINE, MRCK*, MSDS-OHS, NIOSHTIC, PIRA, PROMT, RTECS*, SPECINFO, TOXCENTER, ULIDAT, USPAT2, USPATFULL
(*File contains numerically searchable property data)
Other Sources: DSL**, EINECS**, TSCA**
(**Enter CHEMLIST File for up-to-date regulatory information)



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

1777 REFERENCES IN FILE CA (1962 TO DATE)
10 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
1781 REFERENCES IN FILE CAPLUS (1962 TO DATE)
45 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

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